



Certificate of Analysis

Standard Reference Material[®] 1647d

Priority Pollutant Polycyclic Aromatic Hydrocarbons (in Acetonitrile)

This Standard Reference Material (SRM) is intended primarily as a calibration solution for use in chromatographic methods for the determination of polycyclic aromatic hydrocarbons (PAHs). One unit consists of five 2 mL ampoules, each containing approximately 1.2 mL of an acetonitrile solution of 16 PAHs. The PAHs are the 16 identified by the U.S. Environmental Protection Agency as priority pollutants. This SRM may also be useful in recovery studies for the addition of known amounts of these PAHs to a sample; because the solution is miscible with water, it can be used to fortify aqueous samples with known concentrations of PAHs.

Certified Values and Uncertainties: The certified values of the 16 PAHs are given in Table 1. Values are listed in units of mg/kg (mass fraction) and for user convenience $\mu\text{g/mL}$ (concentration). The $\mu\text{g/mL}$ values were calculated from the mass fraction values using the density of acetonitrile at 23 °C (0.7789 g/mL). An allowance for the change in this density over the range 23 °C \pm 2 °C is included in the uncertainty. The uncertainties are expanded uncertainties at the 95 % level of confidence, calculated according to the International Committee for Weights and Measures CIPM method [1]. They include uncertainty due to the calibration, measurement of the unknown samples, and purity of the materials used to prepare the material. Each certified value and expanded uncertainty define a range of values within which the true concentration is expected to lie with 95 % confidence.

Expiration of Certification: This certification is valid until **31 December 2008**, within the measurement uncertainties specified, provided the SRM is handled and stored in accordance with the instructions given in the certificate (see "Storage and Use"). However, the certification will be nullified if the SRM is damaged, contaminated, or modified. Should any of the certified values change before the expiration of certification, purchasers will be notified by NIST. Return of the attached registration card will facilitate notification.

The coordination of the technical measurements leading to certification was under the direction of L.C. Sander and S.A. Wise of the NIST Analytical Chemistry Division.

Analytical determinations were performed by L.C. Sander of the NIST Analytical Chemistry Division.

Preparation and ampouling of SRM 1647d were carried out by Radian Corporation (now Cerilliant Corporation)¹, Austin, TX.

Statistical design of the experimental work and evaluation of the data were provided by S.B. Schiller of the NIST Statistical Engineering Division.

The support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the Standard Reference Materials Program by B.S. MacDonald of the NIST Measurement Services Division.

Willie E. May, Chief
Analytical Chemistry Division

John Rumble, Jr., Chief
Measurement Services Division

Gaithersburg, MD 20899
Certificate Issue Date: 03 December 2003
See Certificate Revision History on Last Page

¹Certain commercial equipment, instrumentation, or materials are identified in this certificate to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the NIST, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Table 1. Certified Values for PAHs in SRM 1647d

Compound	Mass Fraction (mg/kg)			Concentration ($\mu\text{g/mL}$) (at $23\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$)		
Naphthalene	25.84	\pm	0.33	20.13	\pm	0.32
Acenaphthylene	19.89	\pm	0.32	15.49	\pm	0.29
Acenaphthene	26.67	\pm	0.54	20.77	\pm	0.48
Fluorene	6.09	\pm	0.06	4.75	\pm	0.06
Phenanthrene	4.40	\pm	0.07	3.42	\pm	0.06
Anthracene	1.02	\pm	0.02	0.79	\pm	0.02
Fluoranthene	9.81	\pm	0.11	7.64	\pm	0.10
Pyrene	10.88	\pm	0.11	8.47	\pm	0.11
Benz[<i>a</i>]anthracene	5.25	\pm	0.04	4.09	\pm	0.04
Chrysene	4.71	\pm	0.04	3.67	\pm	0.04
Benzo[<i>b</i>]fluoranthene	5.36	\pm	0.05	4.17	\pm	0.05
Benzo[<i>k</i>]fluoranthene	6.06	\pm	0.07	4.72	\pm	0.07
Benzo[<i>a</i>]pyrene	6.31	\pm	0.09	4.91	\pm	0.08
Dibenz[<i>a,h</i>]anthracene	4.54	\pm	0.27	3.54	\pm	0.22
Benzo[<i>ghi</i>]perylene	4.73	\pm	0.15	3.68	\pm	0.13
Indeno[1,2,3- <i>cd</i>]pyrene	5.49	\pm	0.10	4.28	\pm	0.09

NOTICE AND WARNING TO USER

Toxicity: This SRM contains acetonitrile. Acute and chronic health hazards have been documented from exposure through inhalation, ingestion, and skin absorption. This SRM also contains small amounts of PAHs, some of which have been reported to have mutagenic and/or carcinogenic properties; therefore, care should be exercised during handling and use. Use proper methods for disposal of waste.

INSTRUCTIONS FOR USE

Storage and Use: Sealed ampoules, as received, should be stored in the dark at temperatures between $10\text{ }^{\circ}\text{C}$ and $30\text{ }^{\circ}\text{C}$. Samples of the SRM for analysis should be withdrawn from ampoules and used without delay. The certified values listed in Table 1 apply only to aliquots removed at $23\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$. Certified values are not valid for ampoules which have been stored after opening, even if resealed.

Preparation and Analysis: The acetonitrile solution of the 16 PAHs was prepared gravimetrically from individual compounds. Six of the compounds (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene), were obtained from Radian Corporation¹. The other ten were Certified Reference Materials (CRMs) produced by the Community Bureau of Reference (BCR) Brussels, Belgium and obtained from the Institute for Reference Materials and Measurements (IRMM) Geel, Belgium. The purities of all PAHs used to make this SRM were $\geq 99\%$. Purities of the compounds obtained from the Radian Corporation were determined at Radian by a combination of techniques including differential scanning calorimetry (DSC), gas chromatography with flame ionization detection (GC-FID), reversed-phase liquid chromatography with ultraviolet detection (LC-UV), nuclear magnetic resonance spectroscopy (NMR), and elemental analysis. Purities of CRMs were certified by BCR. The SRM solution was aliquoted into silanized 2-mL amber glass ampoules, which were purged with argon prior to addition of the solution. Samples representing early, middle, and final stages of ampouling were analyzed by LC. No evidence of sample inhomogeneity was observed.

Randomly selected ampoules were analyzed for all 16 PAHs by LC using an acetonitrile-water mobile phase. Concentrations for the 16 PAHs were determined from a straight line calibration, which used gravimetric values and instrumental responses for four calibration standards and three previous issues of this SRM (1647a, b, and c). An internal standard calibration approach was used in the certification. A representative chromatogram and the separation conditions are shown in Figure 1.

Comments on Column Selection: Variations in C₁₈ column selectivity for PAHs are known to result from different column manufacturing processes [2]. Columns prepared by reaction of monofunctional C₁₈ silanes with silica (denoted monomeric C₁₈ phases) differ from columns prepared with silica substrates using trifunctional C₁₈ silanes in the presence of water (denoted polymeric C₁₈ phases). The designation “polymeric C₁₈ column” should not be confused with “polymer substrate columns” (nonsilica columns, often based on polystyrene particles). Better separations of PAH mixtures are often possible on polymeric C₁₈ columns such as that used to produce the chromatogram shown in Figure 1, as compared to monomeric C₁₈ columns. A chromatogram illustrating the separation of the components in the SRM solution using a monomeric C₁₈ column is provided for comparison (Figure 2). Baseline resolution of all components was not achieved with the monomeric C₁₈ column. The classification of monomeric and polymeric C₁₈ columns for the separation of PAHs has been described [2-9] and may be accomplished using SRM 869a, *Column Selectivity Test Mixture for Liquid Chromatography, (Polycyclic Aromatic Hydrocarbons)* [10]. Examples of various C₁₈ columns as “monomeric” or “polymeric” are provided with SRM 869a.

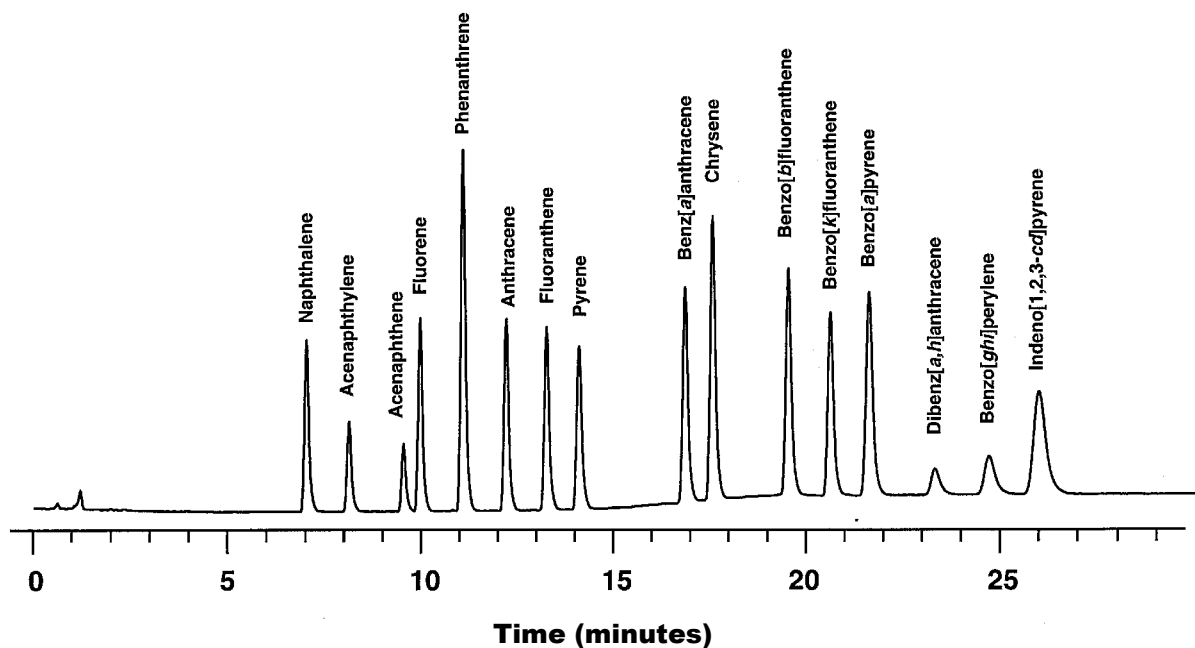


Figure 1. Reversed-phase LC separation of the 16 components of SRM 1647d. A polymeric C_{18} column (Hypersil Green PAH column, 5 μm , 0.46 \times 25 cm; Keystone Scientific¹, Bellefonte, PA) was used with a gradient elution program: 3 minutes hold at 50 % water: 50 % acetonitrile; 15 minutes linear gradient to 100 % acetonitrile; and 15 minutes hold at 100 % acetonitrile.

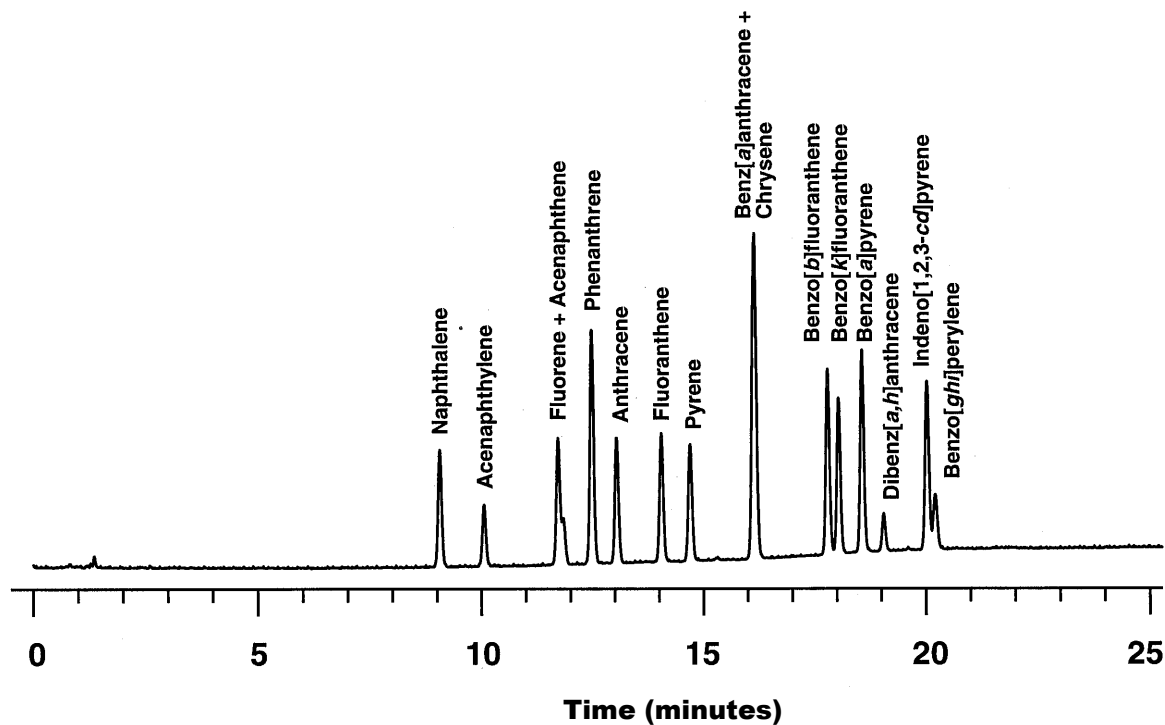


Figure 2. Reversed-phase LC separation of the 16 components of SRM 1647d using a monomeric C_{18} column (Zorbax ODS column, 5 μm , 0.46 \times 25 cm; Mac-Mod Analytical,¹ Inc., Chadds Ford, PA) and the same gradient elution program as in Figure 1.

REFERENCES

- [1] *Guide to the Expression of Uncertainty in Measurement*; ISBN 92-67-10188-9, 1st Ed.; ISO, Geneva, Switzerland (1993); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297; U.S. Government Printing Office: Washington, DC (1994).
- [2] Sander, L.C.; Wise, S.A.; *Evaluation of Shape Selectivity in Liquid Chromatography*; LC-GC, Vol. 8, pp. 378-390 (1990).
- [3] Sander, L.C.; Wise, S.A.; *Investigations of Selectivity in RPLC of Polycyclic Aromatic Hydrocarbons*; Advances in Chromatography, Vol. 25, pp. 139-218 (1986).
- [4] Sander, L.C.; Wise, S.A.; *Determination of Column Selectivity Toward Polycyclic Aromatic Hydrocarbons*; HRC CC, J. High Resolut. Chromatogr. Chromatogr. Comm., Vol. 11, pp. 383-387 (1988).
- [5] Sander, L.C.; Wise, S.A.; *Subambient Temperature Modification of Selectivity in Reversed-Phase Liquid Chromatography*, Anal. Chem., Vol. 61, pp. 1749-1754 (1989).
- [6] Wise, S.A.; Sander, L.C.; *Factors Affecting the Reversed-Phase Liquid Chromatographic Separation of Polycyclic Aromatic Hydrocarbon Isomers*, HRC CC, J. High Resolut. Chromatogr. Chromatogr. Comm., Vol. 8, pp. 248-255 (1985).
- [7] Sander, L.C.; Wise, S.A.; *Influence of Substrate Parameters on Column Selectivity with Alkyl Bonded-Phase Sorbents*; J. Chromatogr., Vol. 316, pp. 163-181 (1984).
- [8] Wise, S.A.; May, W.E.; *Effect of C₁₈ Surface Coverage on Selectivity in Reversed-Phase Liquid Chromatography of Polycyclic Aromatic Hydrocarbons*; Anal. Chem., Vol. 55, pp. 1479-1485 (1983).
- [9] Wise, S.A.; Bonnett, W.J.; Guenther, F.R.; May, W.E.; *A Relationship Between Reversed-Phase C₁₈ Liquid Chromatographic Retention and the Shape of Polycyclic Aromatic Hydrocarbons*; J. Chromatogr. Sci., Vol. 19, pp. 457-465 (1981).
- [10] *Column Selectivity Test Mixture for Liquid Chromatography; (Polycyclic Aromatic Hydrocarbons)*, Certificate; SRM 869a; NIST, U.S. Department of Commerce: Gaithersburg, MD (1998).

Certificate Revision History: 03 December 2003 (This revision reflects an extension of the expiration date); 16 October 1996 (Original certificate date).

Users of this SRM should ensure that the document in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet <http://www.nist.gov/srm>.